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MEASURING pH WITH HIGHLY RESISTANT MEASURING DEVICES

[Following is a translation of an article by Hans Joachim Wolf in the German-language periodical Zeitschrift für Instrumente (Journal of Instruments), Vol 67, No 6, 1959, pages 147-1954.]

In order to understand the peculiarities of electrometer amplifiers for the determination of pH values, the direct coupled d. c. amplifier has been described first. The means which are known at present for the improvement of the connection are mentioned in order to obtain the highest possible stability and measuring accuracy. Furthermore, different systems of modulated amplifiers are shown and practical examples are given. A distinction has been made between direct reading and compensating instruments.

Except for the less exact color indicators for orientation pH determination, modern industry and research relies almost solely upon electrometric measuring methods for pH determination. The most commonly used system is a glass electrode as a pH detector together with a measuring device connected in the manner described below. The total tension of a glass electrode measuring chain is made up of at least four half-elements: the potential building points on the inner and outer glass gelatin layer and the inner and outer reference electrode. Asymmetric potential of the glass gelatin layer and diffusion potential on the diaphragm of the outer reference electrode are also possible. Of these individual potentials, only that on the outer glass gelatin layer which is in contact with the solution to be measured should change its value in accordance with the respective H^+ activity of the solution. Since the thermo-dynamically defined pH value is not accurately measureable in practice, a conventional pH scale, which is based upon the arrangement of certain pH values for so-called calibrating buffer solutions (Primary Standard, for instance 0.05 m potassium biphthalate).

In highly resistant measuring chains such as the glass electrode, the measurement and recording of the pH value places great demands upon the measuring device used. This applies particularly to the input resistance of the measuring device, its accuracy, its linearity and horizontal stability. Due to the high resistance, only instruments with electron tubes come into question at the present time. The electrometric tubes which were used earlier for this purpose because of high grid insulation and good vacuum are now best replaced by normal amplifying tubes. Many devices contain the standard industrial type equivalents of amplifying tubes, some of which have the advantage of a lesser spread factor in addition to a guaranteed life of 10,000 hours.

The tensions of a maximum of several hundred millivolts which are developed in the measuring chain actually require no amplification for actuating a moving coil indicator guage, for instance. But, because of the high resistance, a great power amplification is necessary. Following is a description of one example:

If a voltage of 100 millivolts is applied to a pH meter with an input resistance of 10^{12} Ohms, then the input power is

$$N_E = \frac{U^2}{R} = \frac{10^{-2}}{10^{-12}} = 10^{-14}W.$$

At a voltage increase $V_1 = 1$, a current of 1 mA will be assumed for the meter indicator, therefore

$$N_A = U \cdot J = 0.1V \cdot 1.10^{-3}A = 10^{-4}W.$$

Therefore, in order to have a voltage increase of $V_1 = 1$, the instrument must have a power increase of

$$V_2 = \frac{N_A}{N_E} = \frac{10^{-4}}{10^{-14}} = 10^{10}.$$

Input Resistance

For the following considerations, the resistance of the measuring chain can be assumed to be from 100 to 1000 megohms, which is applicable in most cases. When a measuring instrument is connected to such a measuring chain, a tension division is created with its input voltage; i.e., the voltage at the instrument input E_2 is not equal to the electrode potential E_1 but rather a measuring error of $E_1 - E_2$ results from the input resistance of the instrument, R_E.

Furthermore, a taxing of the electrode by the measuring device with insufficient input resistance could allow a polarization tension to form, which would mean a further error in the value of the electrode potential. The errors could be practically ignored if the input resistance of the measuring device could be made to be two to three times greater than the maximum measuring chain resistance, as

$$R_{input} = 10^{11} \text{ to } 10^{12} \text{ Ohms}.$$

Accuracy

Depending upon the intended purpose, the accuracy of measurement achieved is $\pm$ 0.1 to $\pm$ 0.005 pH. In the case of instruments which give direct reading results, the original measurement error p

caused by inexactness of amplification is compounded by errors of linearity, such as when the instrument indicator does not line up correctly with the scale.

Generally it is required that pH measuring instruments remain constant in their accuracy and linearity even when tubes become old or are replaced.

Stability

Modern pH measuring techniques require electrode calibration through the use of buffer solutions. This creates a demand for a measuring instrument with a scale which is stable throughout a certain period of time, which is usually related to the sensitivity. Allowable variations are expressed in millivolts per hour or of pH per 24 hours. An instrument with a scale stability of several mV per 24 hour period can be considered suitable as a laboratory measuring instrument of average accuracy, especially since the zero point on the scales of these instruments can usually be adjusted. Industrial pH measuring and recording place still higher demands on the stability of measuring instruments. Short interruptions and great variations of circuit tension can be expected in industrial systems. Some of the connections described below meet even these rigid requirements.

Instrument Connection

Directly Coupled Electron Amplifiers

With the advent of grid controlled electron tubes, it was made possible to control the most robust indicating instruments with the smallest measurable amounts of power.

Although the non-linear displacement of the tube characteristic can be taken into account by means of instrument calibration, a considerable inaccuracy of measurement is inherent in this non-linearity, for a variation in the tube characteristics is unavoidable with tube age and tube replacements.

If the indicator instrument is directly in the anode circuit, another sizeable problem results — namely, the loading of the indicator by the anode rest current J_{ao}. The "working point" at the zero point of tension of the tube will be adjusted to the flattest possible part of the characteristic curve by means of the auxiliary grid tension U_g, whereby there is a flow of anode rest current. If it is desired to observe very small measuring tension on the order of several mV, it will be found that the respective anode current change is very much smaller than the anode rest current and is practically not readable. Another disadvantage is more or less characteristic of all directly coupled direct current voltage amplifiers; namely, insufficient time-constancy of the measured value, even with zero input tension. This is mainly due to the influence of variations in the operating power, but even an exceptionally good stabilization of the power supply voltage does not bring absolute stability. A certain straying of the anode rest current will always be observed because of variations in the cathode emission. This instability will appear especially starkly as an inaccuracy when tubes are turned off and then started again. Herein lies the great difference between these and the modulated amplifiers which will be described below, and which can be said to have a practically absolute zero stability.

The first of the above disadvantages of the directly coupled amplifiers -- nonlinearity and characteristic curve displacement, as well as a lessened reading accuracy due to the anode rest current being indicated -- can be eliminated by an appropriate augmentation of the connection. However, this brings only a partial improvement of the zero stability. There is one more point which applies to all directly coupled direct current voltage amplifiers, namely, the existence of a current in the grid circuit.

For all normal amplifying tubes in the usual connection, a grid current of about $1 \cdot 10^{-8}$ amperes can be determined. At a grid resistance of 1 megaohm, a potential of about 10 mV will result due to the grid current. This means an insignificant displacement of the working point. However, if the resistance between the cathode and the grid is increased to a value of 100 to 1000 megaohms, as is caused by the glass electrode, then the grid current can only be allowed to be from 10^{-11} to 10^{-10} amperes if 10 mV is still considered the allowable potential displacement. Such a low grid current can be found in special tubes -- so-called "electrometric tubes," which are plauged by several disadvantages as regards their use in industrial measuring instruments, however, such as their mechanical sensitiveness caused by direct heating and their high price. Modern connection techniques make it possible to use standard amplifying tubes in such a way that their grid current remains under the required minimum values. Prior to going into details of connection, let us take up measures to repress various components of the grid current.

The <u>grid electron current</u> in the residual current stage can be made insignificantly small by means of a negative grid bias for the electrometric connections under consideration here.

The <u>ion current</u> can be avoided only through a good vacuum in the respective tubes. In some cases, suitable tubes must be sought out from among large numbers of the same type.

The <u>insulation grid current</u>, which can result from faulty insulation of the circuit portion grid-cathode, can be avoided in electrometric tubes through mounting another grid at another point, well insulated from the other electrodes. However, one usually experiences little difficulty due to insufficient insulation with present-day standard amplifying tubes which are usually used for pH metering.

Thermic grid emission is greatly dependant upon the cathode temperature and can be repressed through underheating of the tubes. Standard amplifier tubes in electrometric connections therefore usually operate with a heating voltage which is reduced by 10 to 40%.

By taking appropriate measures, therefore, the grid current of certain types of standard amplifying tubes in electrometric connections can be kept below the required value of from 10^{-11} to 10^{-10} amperes.

Techniques of Connecting Directly Coupled pH Amplifiers

The greatest disadvantage of the basic connection was the inaccuracy of measurement caused by the anode rest current being included in the reading. This can be fully compensated for, however, by means of a simple resistance connection, as shown in Figure 1. The instrument indicator of the potentiometer P can be calibrated exactly so that the input tension equals the zero point ($E_I = 0$).

Although a considerable improvement is achieved through the anode rest current compensation, this connection still has many shortcomings, especially due to the fact that the nonlinearity of the tube characteristic curve still is not corrected. The stability of the indicated value and/or the zero point is also poor and strongly dependent upon fluctuations in the heating and anode voltage. There are two measures which can be taken to improve the connection shown in Figure 1 to the extent that it becomes a laboratory type pH meter with satisfactory characteristics. First of all, a second tube system, exactly symmetrical to the original, is connected in place of the stationary resistor R_3. The grid of these tubes is given a tension which is adjustable within certain limits in order to calibrate the zero point, but which is independent of the measuring voltage. Through this symmetrical arrangement, the influence of fluctuating operational voltage is reduced to a fraction of its previous value and the scale stability is considerably better. The second measure consists of powering the tubes in the cathode amplifier connection, whereby a greater linearization of the characteristic curve is obtained. The resulting connection is shown in Figure 2.

The voltage division found in this connection parallel to the anode feed voltage is important in order to be able to adjust the working point (i.e., the correct grid bias to correspond with the minutest grid current) of the tubes.

It should also be noted that stabilization of the heating and anode voltage is mandatory to obtain satisfactory stability in these and similar connections. The following are used as stabilizing means:

neon tubes
magnetic voltage stabilizers
barretters
electron tube regulators
connections with diodes or transistors

A greater improvement is obtained by enclosing both tube systems in a common glass case. This is made possible by the double triodes which are available today, such as ECC 81, ECC 83, E 80 CC.

Other Connections for Directly Coupled pH Measurement Amplifiers

A certain disadvantage to the otherwise well functioning connection shown in Figure 2 is the relatively low power which is available for the meter. This is caused by the fact that, due to low grid tension, they must work with anode rest currents of from 20 to 100 microamperes. A correspondingly high current sensitivity is therefore required in the indicating instrument. Furthermore, since the allowable measuring instrument resistance is limited by the connection, highly sensitive systems must be used which are, in turn mechanically sensitive due to the low torsional moment of their torsion springs. Friction errors in particular can be observed with such sensitive instruments. For this reason, devices have been developed which have a power amplification after the electrometric stage. Robust indicator instruments can then be used, and auxiliary instruments and registering devices no longer offer difficulties. There are basically two methods of providing this power amplification: either the connection of a second, likewise symmetric double triode which, contrary to the first, works with higher anode current, or the use of the so-called modulated amplifier. Figure 4 shows a practical example of the first method.

In the second method, the lowpower direct current which is created between the input cathodes is changed into alternating current by means of a modulator, such as a contact breaker, diode transistor or tube modulator. This alternating current voltage can be greatly amplified with a stabile zero point and later rectified. The connection of one or several indicator instruments with, for instance, 1 milliamphere sensitivity for full registration is possible without difficulty then. Figure 5 shows a block diagram of such an instrument.

Given certain conditions, the modulator can worsen the stability. If a contact breaker is used, provided it has a practical design and correct contact material, no worsening of the stability will be noticed. The disturbance potential created at the contacts, given an exterior resistance of a maximum of several megohms, lies far below 1 millivolt and it is constant. On the other hand, instability can arise through the use of diode and transistor modulators, since these elements are very temperature-sensitive in their electrical characteristics. Symmetric connections and specially selected pairs of elements bring only a partial improvement. Also the electronic modulation by means of a tube bridge is not drift free, but rather functions similarly to a direct coupled direct current voltage amplifier stage.

Many authors recommend the use of the "Cascode" Principle as a possibility of improving the stability of direct coupled direct current voltage amplifiers [7]. This stipulates that an amplifying tube, in place of the usual Ohmic working resistor, contains an additional tube system in the anode or cathode circuit. Figure 6 describes this further. However, the author does not know of any commercial pH measuring devices which use this principle.

Directly Coupled Measurement Amplifiers With External Counter-Coupling

The cathode amplifier, as shown in Figures 2-4, represents an internally counter-coupled tube connection. In contrast to this, we speak of an external counter-coupling when the back feeding of the counter-coupled voltage takes place into the amplifier lead in via several tube stages. Such connections are used in some modern pH measuring devices. They have certain advantages over the instruments shown in Figures 2-4, but do not by any means represent an ideal solution. Their advantage, for instance, consists of the fact that the zero point fluctuation is caused, for the most part, only in the input stages. The influence of subsequent tube stages is reduced by the factor of the amplification in the intervening portion. Additional advantages can be noted in the speed of adjustment and the exactness of amplification. However, these stated advantages apply only in the case of sufficiently great interior amplification, that is to say, strong counter coupling. The characteristics of such an amplifier can be expressed with the help of Figure 7:

In order to obtain the above mentioned advantages, it must be given: $a \cdot V_1 \approx 100$ to 1000 (as great as possible).

When external counter coupling is used, the same viewpoints apply for the input stage as regards grid current as are given for the simple connection. In this situation, therefore, counter coupling has no advantages.

A disadvantage of such connections is the complicated potential relationship within the amplifier, as necessarily results when more then two directly coupled tube stages which are connected in series and fed from a common anode voltage source. An electronic voltage regulator should be used to produce the relatively high operating voltage necessary for this, to include the power required for a strong voltage divider. Thus a considerably greater source is needed than for the connections shown in Figures 2-4. This is compensated for by only a partial improvement.

The feed in of the counter coupled voltage can actually be done at another point besides the input stage, as is shown in Figure 7. An electrometric measuring amplifier has been described [9] in which the counter coupling passes via the heating of the directly heated electrometric input stage. The method is seen in the simplified scheme shown in Figure 8. The attainable zero point stability is stated to be 0.15 millivolt per hour.

Directly Coupled Measuring Amplifiers With Automatic Drift Compensation

PH measuring devices which use this principle represent a specialty in the developmental series of directly coupled direct current amplifiers. The manner of functioning of the automatic, intermittent drift control can be explained with the help of Figure 9.

A voltage amplification factor of $v = 1$ is assumed for the amplifier, which corresponds to a counter coupling factor of $a = 1$ for a counter coupled amplifier. During the measuring phase, three voltages, which are connected in series, lie at the input: the measuring voltage E_x, the voltage of the condensor U_o and a disturbance voltage U_{st} which corresponds to a zero point displacement (drift). During the "control phase," E_x is diverted and the condensor is loaded to the drift voltage U_{st} (in the opposite direction) via the amplifier. If the time constant C of the condensor is sufficiently large and if the amplifier input is correspondingly highly resistant, then the loading of C will fully compensate the disturbance voltage U_{st} during the next measuring phase. With a commercially available pH meter, the measuring phase lasts 1 second, whereas the drift control is completed in 0.015 second.

This process places certain demands on the exact functioning of the switch contacts. For this reason, and largely because of the high resistance of the input, a special relay is required. There is no known experience factor concerning the suitability of this measuring principle for precision pH meters.

pH Measuring Devices with Modulated Amplifiers

General

Here the changing of the electrode potential into alternating current voltage takes place directly, as opposed to the devices similar to Figure 4. All tubes work as alternating current voltage amplifiers in standard connection, thus being zero point stabile and unaffected by grid currents. A good measuring accuracy and linearity, as well as the required high input resistance, is obtained through a powerful counter coupling.

The same relationships apply as for the directly coupled amplifier with external counter coupling. The attainable input resistance is dependent upon other factors, however, since no grid current effect occurs. The increase of the input resistance takes place, in modulated amplifiers, according to the ratio

$$R_e = R_e'(1 + a'V_1)$$

where

R_e' = input resistance without counter coupling

R_e = input resistance with counter coupling

a = Counter coupling factor (actually 0.1 - 1)

V_1 = internal amplification $V_1 = E_2/E_1$

If $R_e' = 250$ megaohms and the effective input resistance should, considering the highly resistant measuring chain, amount to $1 \cdot 10^{11}$ Ohms, then $a \cdot V_1 = R_e/R_e'$ must equal 400. For stability of measurement accuracy and linearity, a sufficiently great $a \cdot V_1$ is also important and renders the device practically independant of tube age, tube replacement and grid voltage fluctuation. From

$$E_2 = \frac{E_x}{1 + 1/V_1}$$

(given a counter coupling factor $a = 1$) it can be seen that with sufficiently great V_1, the numerator practically disappears and $E_2 \approx E_x$ results. Depending upon the choice of the counter coupling factors, values of $V_1 = 100$ to 10,000 are required. A dropping of V_1 of 50%, as from $V_1 = 1000$ to $V_1 = 500$, results in no visible indicator change.

Instruments with Vibrators or Oscillating Condensors

At the present time, the contact vibrator and the oscillating condensor are the most important modulators in practice. Figure 11 shows typical input connections.

The doubled G-R link at the tube grid serves to keep the voltage which results from grid current between the grid and "minus" from entering the modulator.

With vibrators, the disturbance voltage caused by the contact potential is most noticeable and impossible to eliminate completely. This disturbance voltage depends upon the value of the external resistance, the contact material, the cleanliness of the contact surfaces and the frequency of the vibrator. Certain gold alloys have proven themselves a contact material, but greater improvement is hardly to be expected in this area. By reducing the frequency of the vibrator, this potential can be reduced approximately proportionately. However, there is a limiting factor if the measuring amplifier is required to follow rapid changes in the measured value. Well known pH meters therefore use only 50 or 25 cycle vibrator frequencies. The advantage of a smaller contact potential with the 25 cycle vibrator brings with it large disadvantages, for a frequency reducer is required as well as a second vibrator which is used as a rectifier. As example of the values of contact potentials with contact vibrators, a pH meter which works with 50 cycle vibrator showed a contact potential of 2 to 10 millivolts at a measuring chain resistance of 1000 megohms.

The oscillating condensor also has a disturbance voltage, which is also called a contact potential. Of greatest importance is the type of material and the surface of the plates. They can achieve satisfactory results with gold plated and dust free arrangements. There are also some known oscillating condensors which are hermetically sealed and operate partly in a protective gas atmosphere. However, such types hardly come into question as industrial pH meters because of their prohibitive cost. Contrary to the contact vibrator, a high frequency, such as 400 cycles, can be beneficial in some cases. The values of the contact potential are higher with the simple models than with the vibrator and can amount to as much as 50 millivolts at 1000 Megohms. A further increase to unallowable high values can occur after several months of continuous operation.

Electronic Modulation

In principle, an electronic tube can serve to transform direct measuring current voltage into a proportional alternating current voltage. Such connections, which usually work with a tube bridge arrangement, have been variously described [8]. Their importance for pH meters is not great today, however, since they are plagued by the same drift characteristics as are known with directly coupled amplifiers.

"Two Channel Amplifier"

Directly coupled direct voltage current amplifiers and modulated amplifiers can be combined with each other in such a way that the advantages of both systems can be utilized. The combination is as follows: rapid changes in the measured valued are passed through the directly coupled channel, while slow fluctuations (drift) are corrected in a slow-running vibrator amplifier. If the frequency of the vibrator is only 5 cycles, for instance, then its contact potential is so small that the measurement of the most highly resistant measuring chains — up to 2000 megohms — becomes possible [10].

V_1 is the directly coupled main amplifier which is affected by the disturbance voltage. Its output voltage E_2 is fed back into the input via the counter coupling circuit a with a $\cdot$ E_2. Up to this point, the same conditions exist as with the amplifier in Figure 13 — that is, the disturbance voltage u, which is always present and is caused by drift and other causes, appears at its fullest value. The external voltage is 1/a. By comparing the measuring voltage E_x with that portion of the fed back voltage a · E_2, the value of u is obtained. u is then fed to the correcting amplifier V_2. In the form of a slowly operating vibrator amplifier, its disturbance voltage will be so minimal as to be ignored. An exact examination reveals that the disturbance voltage of the main amplifier u is reduced by the factor $1/V_2$ if the output voltage V_2 is fed back to the main amplifier input with the correct phase. With sufficient stabilization of V_2, the stability becomes extraordinarily good, so that this principle is suitable for pH measuring amplifiers in spite its great cost.

Principle of Compensation

The most reliable method for measuring electrochemical potentials is compensation. The voltage to be measured is placed opposite a polarity which is adjusted to be the reverse of the voltage, and then alternated until the voltage difference is zero. The accuracy of this type measuring instrument is dependant only upon the precision of the resistors used and the accuracy of calibration of the voltage source. A standard element is often used as a calibrating standard, while a highly stabilized circuit rectifier is used as the compensation voltage source. In older instruments, a battery or the standard element itself is used. We differentiate between self-equalizing compensators and those with which the equalizing must be done manually. For the best accuracy, manual compensation is preferred.

Compensating Measuring Devices With Manual Equalizing

The basic connection requires certain additions in order to be able to measure highly resistant potential sources.

This applies particularly to the zero indicator, since practically no power is available due to the high resistance of the measuring chain. A direct reading moving coil instrument is therefore not suitable. The necessary tube amplifier can be either directly coupled or constructed like a modulated amplifier. For purposes of obtaining the greatest possible accuracy, the latter should be given preference since it possesses the possibility of attaining a high, zero-point-stabile voltage amplifier. Figure 13 shows a block diagram of such a compensator.

The modulated amplifier used with this device provides a voltage amplification so strong that the zero indicator uses magic eye difference voltage of less than 0.5 millivolts and gives very definite registrations. The measuring of electrode-chains up to 1000 megohms is quite possible.

Self-Equalizing Compensators

The equalization is best accomplished with a servo motor. In order to obtain sufficient accuracy with rapid adjustment — 1 or 2 seconds for the full range — a damping generator or a special connection with a corresponding function is absolutely necessary.

The servo motor runs and adjusts the potentiometer sliding contacts so long until the difference voltage $E_1 - E_x \pm E_2$ (see Figure 13) approaches zero. The attainable adjustment accuracy therefore depends upon the available degree of amplification. On the other hand, amplification cannot be increased to any desired height, or the entire system would begin oscillation. Limits are set to the stability attainable with the damping generator or correspondingly functioning connection. The adjustment accuracy attainable with standard means with such instruments is therefore usually given as 0.2 to 0.3% of the final value. 50 cycles is the usual modulation frequency since it is easiest to connect the second motor winding, which is fed with alternating current voltage, directly to the circuit.

Self-equalizing compensators are usually designed as registering instruments, since the driving power of the servo motor is easily sufficient to drive an inscribing stylus.

Figure 14 shows a modern compensator graph. For automatically recording the titration curves, the paper advancer is combined here with the piston burette. The instrument uses a common ball point insert and has a usable recording width of 250 mm. Adjustment is rapid and accurate.

Summary

The problem of mass producing the above described special tubes which are reliable in continuous operation can be considered as having been solved.

pH measuring devices can be divided according to type into two main classes. In the first group, the measuring voltage is fed directly to the indicator dial after amplification. A directly coupled or a modulated amplifier can be used, a combination of both also being possible. The second main group works on the compensation principle. The measuring voltage is placed opposite a variable, calibrated compensation voltage and alternated until the difference voltage is zero. The control of the compensation current can be manual or automatic by means of a servo mechanism, the latter method often being combined with a registering device (compensograph).

A special class are the direct reading devices, in which the measuring voltage is partially compensated by an adjustable, staged counter current. The device shown in Figure 3 works on this principle. In connection with these instruments, one speaks of "partial compensation."

Measuring amplifiers with external counter coupling can also be considered as self-equalizing compensators. From these considerations, there results the above mentioned increased accuracy and — in the case of the modulated amplifier — the magnification of the input resistance.

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FIGURE APPENDIX

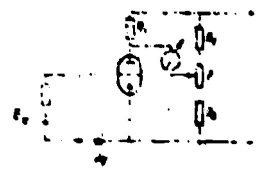


Fig. 1. Principle of anode rest current compensation.

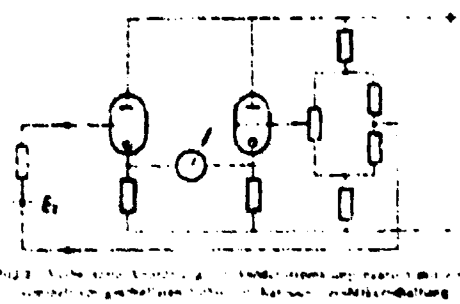


Fig. 2. Improved arrangement for anode current compensation with two symmetrically connected tubes and cathode amplification connection.

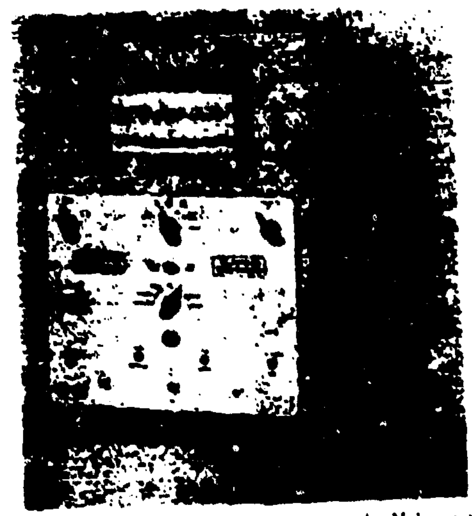


Fig. 3. Precision pH meter with partial compensation of the measuring voltage. All operating voltages are electronically stabilized (Metrohm Corporation, Herisau, Switzerland).

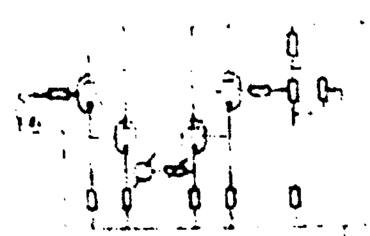
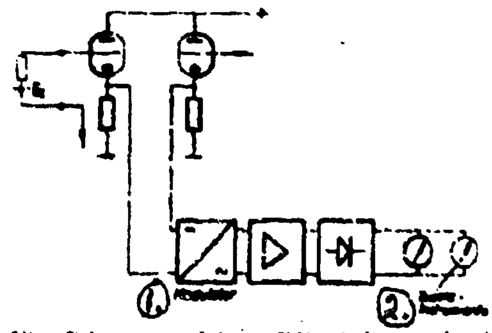


Fig. 4. Wiring scheme of an arrangement with an electrometric and a power amplification stage.



1. Modulator
2. Additional instruments

Fig 5. Block diagram of an instrument with electrometric input stage and subsequent power amplification by means of modulated amplifier.

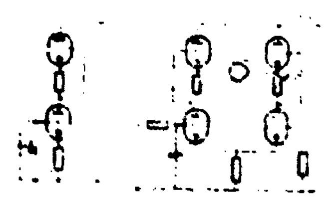


Fig 6. Left: Cascode Principle. Right: Symmetric direct current voltage amplifier in a Cascode arrangement.

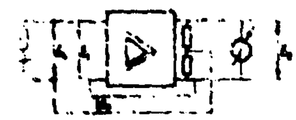


Fig. 7. Counter coupled amplifier. $E_1 = E_2 - E_3$

Interior amplification $\quad V_1 = \frac{E_2}{E_1}$

External amplification $\quad V_a = \frac{E_2}{E_x}$

Counter coupling factor $a = \frac{E_3}{E_2}$ (practically, a = 0.1-1)

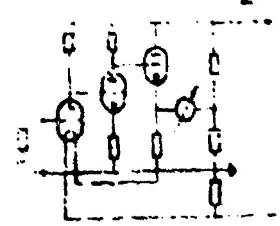


Fig. 8. Counter coupling via the heating of the directly heated electrometric input stage.

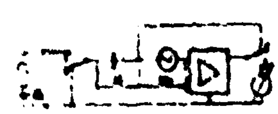


Fig. 9. Principle of the intermitent drift compensation
I: Measurement phase
II: Contml phase

p

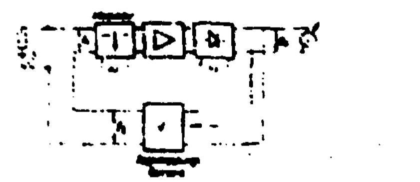


Bild 10 Modulierter Verstärker mit äußerer Gegenkopplung

Fig 10. Modulated Amplifier with External Counter coupling

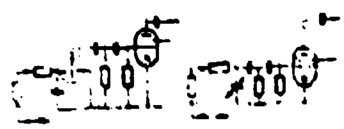


Fig 11. Input connections, a) with vibrator, b) with oscillating condensor.

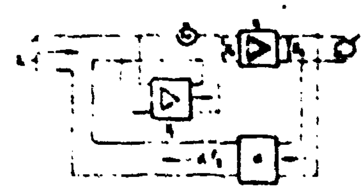
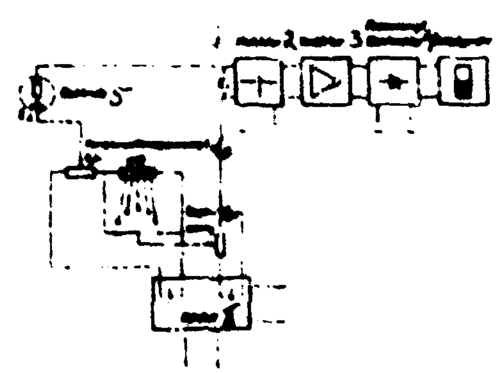


Fig 12. Two channel amplifier.



1. Modulator
2. Amplifier
3. Phase-sensitive rectifier
4. Indicator dial
5. Electrode
6. Compensation voltage E_2
7. Back feed voltage
8. Cathode

Fig. 13. Block diagram of a precision compensator.

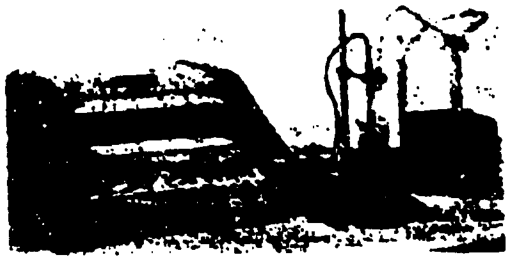


Bild [illegible]. [illegible] zur [illegible] des [illegible]
Meßketten [illegible] mit [illegible] und [illegible]
[illegible] Aufnahme von [illegible]
[illegible] AG Herisau [illegible]

Fig. 14. A compensatograph for registering the potential of highly resistant measuring chains. A combination of piston burette and magnetic scribe for the automatic recording of the titration curves (Mètrohm Corporation. Herisau, Switz.).